

# PATENT SPECIFICATION

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## PROVISIONAL SPECIFICATION.

### Improvements in or relating to the Manufacture of Rubber or Ebonite and Articles Composed thereof.

We, UGO PESTALOZZA, an Italian Subject, and SOCIETA ITALIANA PIRELLI, a Body Corporate organised under the laws of the Kingdom of Italy, both of 21, Via Fabio Filzi, Milan, Italy, do hereby declare the nature of this invention to be as follows :—

This invention is for improvements in or relating to the manufacture of rubber or ebonite having a cellular or sponge-like structure and articles composed of such rubber or ebonite, from aqueous dispersions of natural or synthetic rubber.

According to the present invention, a process for the manufacture of cellular rubber or ebonite or articles composed thereof, from aqueous rubber dispersions, is characterised by gasifying the dispersion during coagulation thereof, with or without continuing the gasification after coagulation, by effecting fermentation of material in the mass with evolution of gas therein.

More specifically, the invention includes a process as aforesaid, characterised by intimately admixing with a dispersion of rubber, for example, rubber latex, a solution of a fermentable substance and a solution or suspension of a ferment or its active principles, the fermentable substance and ferment being of a character such that gas is evolved by the fermentation which is insoluble or only slightly soluble in the dispersion medium.

According to a further feature of the invention, the latter may comprise, if necessary, the additional step of heat-treating the cellular coagulum to rupture the walls of the cells thereof and thereby render them intercommunicating with one another.

The invention further includes, in the case of vulcanised cellular rubber or ebonite, the step of heat-treating the cellular coagulum to effect vulcanisation thereof, for example, the parent rubber dispersion from which the coagulum is produced having vulcanising agents incorporated in it.

The cellular coagulum which is obtained in the process contains more or less serum from the parent dispersion, which, for [Price 1s.]

most purposes, requires to be eliminated from the coagulum by a drying operation. This may conveniently be permitted to take place during the heat-treatment step referred to above.

Moreover, in the case of a vulcanised product obtained by heat vulcanisation of the cellular coagulum, the rupture aforesaid of the walls of the coagulum cells may be effected during the heat vulcanisation step.

Any suitable combination of fermentation-producing substances may be used for the purposes of this invention, for example, glucose, cane sugar, beet sugar, molasses or the like, as a fermentable substance, and the saccharomyces of yeast as a ferment.

As will be appreciated, however, it may be necessary somewhat to adjust the alkalinity or acidity of the parent rubber dispersion to suit the conditions of activity of the ferment used. For example, if the parent rubber dispersion be ammonia-preserved latex, the fermentable substance chosen be one of those specifically mentioned above and the ferment be a saccharomyce of yeast, the greater part of the preservative ammonia from the latex will need to be removed in order not to render inactive the ferment.

By operating upon rubber latex, for example, latex concentrated to a 50 per cent. dry rubber content, and using as the fermentation-producing substance one of the specific fermentable substances mentioned above and a yeast saccharomyce, the latex having first been depauperated of preservative ammonia the latex mix, upon being left to stand at a suitable temperature so that fermentation proceeds in the mass, first transforms into a non-homogeneous semi-coagulum of mud-like consistency, due to the action of carbon dioxide evolved in the mass by the fermentation therein, and thereafter as fermentation proceeds and further carbon dioxide gas is evolved, the mass swells with the formation in its interior of irregularly shaped cavities uniformly distributed through the coagulum.

According to another feature of the invention, a coagulant may be added to

the parent rubber dispersion, its effect being added in the process to the coagulating effect (if any) of the fermentation gas evolved in the mass.

5 Thus, for example, rubber latex, previously freed substantially from ammonia may have added to it a suitable coagulant in a quantity less than that requisite to produce immediate coagulation and such  
10 that the coagulum which forms during fermentation of the fermentable material within the mass will first be substantially homogeneous and compact, whereupon by continuing the fermentation within the  
15 mass, the latter is caused to swell, due to the further evolution of gas within it.

The swollen mass of coagulum which is produced when this procedure is followed  
20 is of a cellular structure, composed of uniformly distributed cells having very thin walls which can readily be ruptured by the application of heat to the coagulum.

25 With regard to the choice of a coagulant for use in the process, it may be remarked that, substantially speaking, any of the known coagulants for rubber latex may be employed provided they are  
30 not capable of killing the ferment. A very suitable coagulant is magnesium sulphate. This particular coagulant can be introduced into rubber latex, even in considerable quantity, without fear of premature coagulation taking place, by  
35 gently stirring into the latex an aqueous solution of the sulphate containing a dissolved ammonium salt, for example, ammonium sulphate, in sufficient quantity  
40 to prevent the immediate formation of precipitates within the latex produced by the action of the dissolved magnesium salt upon the albumins and other dissolved substances in the serum of the  
45 latex.

It is found that within fairly narrow limits the ultimate degree of cell formation or sponginess increases with the  
50 quantity of fermentable substances introduced into the latex; in other words, the ratio of the final volume of the fermented mass to the initial volume of parent dispersion increases more or less with the quantity of fermentable substance introduced  
55 into the latex. This holds good up to a certain point, beyond which, further addition of fermentable substance is without appreciable effect.

Further, in this connection, an increase  
60 in the quantity of ferment added to the latex, the quantity of fermentable substance remaining the same, at first gives rise to an increase in the ratio aforesaid between the final volume of the fermented  
65 mass and the initial volume of parent

latex used in its formation, then to a steady or unaltered condition of the ratio and finally to a reduction thereof.

A similar effect is produced by varying the quantity of coagulant incorporated into the latex. Thus, adding to  
70 the latex quantities of coagulant gradually increasing above the minimum quantity which is required to produce, as a result of the fermentation, a regularly  
75 cellulated mass, the value of the ratio referred to first increases and then rapidly decreases, while the coagulum becomes more and  
80 more hard, and the tendency of the serum to separate from the coagulum increasingly pronounced.

The precise quantities of fermentable substance and ferment in any given  
85 actual application of the invention, as also the most appropriate quantity of coagulating agent to be employed, will, in general, vary with the kind of rubber dispersion in hand, and with the water-content of the dispersion.  
90

These quantities, however, can be readily determined by simple preliminary test.

The parent rubber dispersion may contain vulcanising and coagulating agents  
95 as already indicated, and in addition to these agents, if desired, fillers, dyestuffs, anti-oxidants or other addition substances common in the industry. It is to be appreciated, however, that care  
100 should be exercised to avoid the use of addition substances, notably certain accelerators, anti-oxidants and organic dyestuffs, the presence of which in the dispersion would tend to poison or weaken  
105 the action of the ferment.

It is found that when sugars are used as the fermentable substance in conjunction with brewing ferments, the presence  
110 of sulphur for vulcanisation in the parent dispersion gives rise to the formation of hydrogen sulphide in the mass, this sulphide being evolved in addition to the carbon dioxide evolution from the fermentation. When a large quantity of  
115 sulphur is incorporated in the dispersion, for example, a quantity sufficient to result in the formation of ebonite, hydrogen sulphide is formed almost exclusively and only small quantities of carbon dioxide  
120 are evolved; and conversely when only small quantities of sulphur are present, for example, such small quantities as are usually requisite to obtain soft rubber, the formation of hydrogen sulphide is  
125 correspondingly small and the evolution of carbon dioxide prevails, the amount of hydrogen sulphide formed being so small as to be readily capable of being bound, if necessary, by small quantities of zinc  
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oxide suspended in the dispersion.

If the mix of parent rubber dispersion and fermentation substances contains only small quantities of added ingredients, for example, only vulcanising agents and zinc oxide, the bubble cells at the completion of fermentation may be of relatively large dimensions and the final elastic mass of cellular rubber may in consequence be incapable of quickly regaining its initial volume upon being compressed.

By incorporating a finely divided insoluble inert substance into the latex, however, for example, finely ground glass, pumice stone or siliceous material, the small particles of the incorporated substance function as centres or initiators of bubble formation and in this way, a vulcanised product may be produced which is highly resilient and constitutes an excellent sponge rubber, its cells being small and very regularly distributed.

It may further be remarked in this connection that the small and regularly distributed bubble cells which are produced in this manner readily intercommunicate with one another by rupture of their walls, after the step of vulcanising the coagulum, by heating the mould in which the fermentation has taken place.

In the contrary event, of additional finely divided solid matter, such as that referred to, being absent from the parent dispersion, the intercommunication of the bubble cells can be produced, either by immersing the fermented mass in boiling water for a sufficient time, vulcanising it, if necessary, at the same time, or by subjecting the coagulum to the action of a vacuum. The latter mode of operation may be carried out, either at room temperature, in which event subsequent heat treatment of the mass will be required to obtain a vulcanised product, or, alternatively, at an elevated temperature, the duration of the heat-treatment, in this case, being sufficient to effect, at the same time, dehydration and vulcanisation of the mass.

The quantity of bubble-promoting suspended solid matter in the dispersion may vary within fairly wide limits, for example, between 4 per cent, and 20 per cent, reckoned on the dry rubber content of the dispersion. In general, the higher the percentage of added solid matter employed, the more numerous and small will be the bubble cells in the finished product.

In the case of parent dispersions containing, for example, for the production of ebonite, relatively large quantities of sulphur, it may be unnecessary to incor-

porate additional finely divided solid matter in the dispersion for the promotion of bubble formation, or at any rate such large quantities thereof as would otherwise be necessary as in this case the evolution of gas occurs in the form of an exceedingly large number of small bubbles distributed throughout the mass of dispersion. This effect is probably due, either to the peculiar character of fermentation which occurs in the conditions contemplated, resulting, as stated, in the evolution of hydrogen sulphide in place of carbon dioxide, or to the presence in the dispersion of fine crystals of sulphur distributed through the mass and operating as initiating centres of bubble formation.

In this case also, after vulcanisation, the bubble cells are brought into intercommunication with one another upon application of heat or vacuum in the manner referred to above.

When the final products are of elastic rubber, such in general as those contemplated in the first of the following examples, a substantial decrease in volume of the bubble cells tends to occur during the drying of the coagulum, due to the contraction of the separating walls of the cells (which, as will be appreciated, are composed of more or less highly hydrated rubber) and, in consequence, the resulting final products are more compact than the freshly formed coagulum and the cells may shrink in a somewhat irregular manner. We have found, however, that this effect may be avoided, if necessary, by preventing the outer surfaces of the mass of coagulum, as it is being dried and vulcanised, from contracting and thereby preventing general shrinkage of the cellular mass. By this means, the separating walls of the interior cells of the mass are compelled to dry without undergoing deformation or decrease in surface area and the initial open cellular structure of the wet coagulum is substantially preserved in the finished product.

One method of carrying this feature into effect consists in removing the fermented mass from the mould in which fermentation has taken place, preferably prior to the step of vulcanising the mass, and placing it into another mould, the walls of which are composed, like a cage, of metal network and have been previously coated with rubber solution or a like suitable adhesive. The cellular mass having been placed within this second mould, is then heated to vulcanise the component rubber. After this step, which can be carried out by placing the mould

or cage into a closed container and immersing the whole into boiling water, the mould is immersed for a few hours in cold water in order to cleanse the rubber within it, after which, still in position within the network cage, the cellular mass is dried, either in a vacuum or in a heated oven. Finally, the dried product is removed from the network mould and constitutes the finished product of the process.

As to the temperature to obtain in the fermentation step of the process, the most appropriate range of temperatures for most combinations of fermentable substances and ferment, is from 25° to 36° C. When operating at 30°—31° C. a dispersion containing the usual rubber mix ingredients and a small quantity of sulphur, for example, 2 to 7 per cent. reckoned on the dry rubber content of the mix, a maximum increase of superficial volume of the dispersion is reached in 6 or 7 hours the final volume then being about 4—5 times the initial volume of the parent mix. In the case of a mix containing a relatively high proportion of sulphur, for example, a proportion sufficient for the production of ebonite, the time required to attain maximum volume increase is considerably longer than in the former case, for example, twice as long, and the ultimate superficial volume reached somewhat less, for instance, only about 3—5 times the initial volume of the dispersion.

Generally speaking, as already stated, it is advisable, if not essential, substantially to free the rubber dispersion of ammonia before adding the fermentation materials, and it is probably equally important to ensure that decomposition of the proteins in the latex has not already begun when these materials are added.

According to a further feature of the invention, moreover, the actual degree of volume increase (or sponginess) in the cellulation of the dispersion may be controlled and predetermined by selecting a mould of an internal volume corresponding to the desired final volume of the coagulum and having in it, for example, at the top, an exit for the air displaced by the swelling of the mass, or for the escape of excess gas from the fermentation, and introducing into this mould for coagulation and fermentation therein just that quantity of parent dispersion which upon completion of fermentation will occupy the whole of the interior of the mould.

The invention will now be illustrated by way of example in the following Examples.

#### EXAMPLE I.

A parent rubber dispersion was prepared as follows:—

To 100 grams of latex, concentrated to 50 per cent. dry rubber content and freed from ammonia, there were added:

10 c.c. of a 50 per cent. solution of sugar having admixed with it 2 grams of yeast.

1.5 grams of crystallised magnesium sulphate and 1.5 grams of ammonium sulphate dissolved in 10 c.c. of water.

15 c.c. of a 5 per cent. aqueous solution of glue containing suspended in it 1 gram of sulphur, 0.5 grams of zinc dimethyldithiocarbamate, 0.2 grams of zinc oxide and 2 grams of very finely ground pumice stone.

This dispersion was left to ferment in a suitable mould for about 6 hours at about 30° C. The fermented mass was then removed from the mould and enclosed in another mould or cage having metallic mesh walls which had been previously coated with rubber solution. The second mould was placed in a closed container and the whole submerged into boiling water where it was left for about one-and-a-half hours for vulcanisation. During this step, the exterior surfaces of the mass remained steadily adhered to the network walls of the mould. The cage was then removed from the closed container and submerged for some hours in cold water, whereupon the mass was dried in a heated oven and the resulting final mass of sponge rubber was separated from the cage.

#### EXAMPLE II.

A parent dispersion for the production of sponge ebonite was prepared as follows:—

To 100 grams of latex of 50 per cent. dry rubber content previously freed from ammonia, there were added:

15 c.c. of a 50 per cent. solution of sugar containing admixed with it 1 gram of yeast.

4 grams of crystallized magnesium sulphate and 4 grams of ammonium sulphate dissolved in 35 c.c. of water.

20 c.c. of a 5 per cent. aqueous solution of glue containing suspended in it 17 grams of sulphur.

This dispersion was left to ferment in a suitable mould for about 6 hours at about 30° C. The mould containing the fermented mass was then heated in an autoclave for about 8 hours at a pressure of about 3 atmospheres (for example 143° C.) to effect vulcanisation of the mass. The final product was sponge ebonite having a very regular cellular structure.

Dated this 21st day of May, 1932.

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Agents for the Applicants.

## COMPLETE SPECIFICATION.

**Improvements in or relating to the Manufacture of Rubber or Ebonite and Articles Composed thereof.**

We, UGO PESTALOZZA, an Italian Subject, and SOCIETA ITALIANA PIRELLI, a Body Corporate organised under the laws of the Kingdom of Italy, both of 21, Via Fabio Filzi, Milan, Italy, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention is for improvements in or relating to the manufacture of rubber or ebonite having a cellular (e.g. sponge-like) structure and articles composed of such rubber or ebonite, from aqueous dispersions of natural or synthetic rubber.

According to the present invention, a process for the manufacture of cellular rubber or ebonite or articles composed thereof, from aqueous rubber dispersions, is characterised by gasifying the dispersion during coagulation thereof, with or without continuing the gasification after coagulation, by effecting fermentation of material in the mass with evolution of gas therein.

More specifically, the invention includes a process as aforesaid, characterised by intimately admixing with a dispersion of rubber, for example, rubber latex, a solution of a fermentable substance and a solution or suspension of a ferment or its active principles, the fermentable substance and ferment being of a character such that gas is evolved by the fermentation which is insoluble or only slightly soluble in the dispersion.

According to a further feature of the invention, the latter may comprise, if necessary, the additional step of heat-treating the cellular coagulum to rupture the walls of the cells thereof and thereby render them intercommunicating with one another.

The invention further includes, in the case of vulcanised cellular rubber or ebonite, the step of heat-treating the cellular coagulum to effect vulcanisation thereof, for example, the parent rubber dispersion from which the coagulum is produced having vulcanising agents incorporated in it.

The cellular coagulum which is obtained in the process contains more or less serum

from the parent dispersion, which, for most purposes, requires to be eliminated from the coagulum by a drying operation. This may conveniently be permitted to take place during the heat-treatment step referred to above.

Moreover, in the case of a vulcanised product obtained by heat vulcanisation of the cellular coagulum, the rupture aforesaid of the walls of the coagulum cells may be effected during the heat vulcanisation step.

Any suitable combination of fermentation-producing substances may be used for the purposes of this invention, for example, glucose, cane sugar, beet sugar, molasses or the like, as a fermentable substance, and the saccharomyces of yeast as a ferment.

As will be appreciated, however, it may be necessary somewhat to adjust the alkalinity or acidity of the parent rubber dispersion to suit the conditions of activity of the ferment used. For example, if the parent rubber dispersion be ammonia-preserved latex, the fermentable substance chosen be one of those specifically mentioned above and the ferment be a saccharomyce of yeast, the greater part of the preservative ammonia from the latex will need to be removed in order not to render inactive the ferment.

By operating upon rubber latex, for example, latex concentrated to a 50 per cent. dry rubber content, and using as the fermentation-producing substance one of the specific fermentable substances mentioned above and a yeast saccharomyce, the latex having first been depauperated of preservative ammonia the latex mix, upon being left to stand at a suitable temperature so that fermentation proceeds in the mass, first transforms into a non-homogeneous semi-coagulum of mud-like consistency, due to the action of carbon dioxide evolved in the mass by the fermentation therein, and thereafter as fermentation proceeds and further carbon dioxide gas is evolved, the mass swells with the formation in its interior of irregularly shaped cavities uniformly distributed through the coagulum.

According to another feature of the invention, a coagulant may be added to

the parent rubber dispersion, its effect being added in the process to the coagulating effect (if any) of the fermentation gas evolved in the mass.

5 Thus, for example, rubber latex, previously freed substantially from ammonia, may have added to it a suitable coagulant in a quantity less than that requisite to produce immediate coagulation and such  
10 that the coagulum which forms during fermentation of the fermentable material within the mass will first be substantially homogeneous and compact, whereupon by continuing the fermentation within the  
15 mass, the latter is caused to swell, due to the further evolution of gas within it.

The swollen mass of coagulum which is produced when this procedure is followed is of a cellular structure, composed of  
20 uniformly distributed cells having very thin walls which can readily be ruptured by the application of heat to the coagulum.

With regard to the choice of a  
25 coagulant for use in the process, it may be remarked that, substantially speaking, any of the known coagulants for rubber latex may be employed provided they are not capable of killing the ferment. A very  
30 suitable coagulant is magnesium sulphate. This particular coagulant can be introduced into rubber latex, even in considerable quantity, without fear of premature coagulation taking place, by  
35 gently stirring into the latex an aqueous solution of the sulphate containing a dissolved ammonium salt, for example, ammonium sulphate, in sufficient quantity to prevent the immediate formation  
40 of precipitates within the latex produced by the action of the dissolved magnesium salt upon the albumens and other dissolved substances in the serum of the latex.

45 It is found that within fairly narrow limits the ultimate degree of cell formation or sponginess increases with the quantity of fermentable substances introduced into the latex; in other words, the  
50 ratio of the final volume of the fermented mass to the initial volume of parent dispersion increases more or less with the quantity of fermentable substance introduced into the latex. This holds good up  
55 to a certain point, beyond which, further addition of fermentable substance is without appreciable effect.

Further, in this connection, an increase in the quantity of ferment added to the  
60 latex, the quantity of fermentable substance remaining the same, at first gives rise to an increase in the ratio aforesaid between the final volume of the fermented mass and the initial volume of parent  
65 latex used in its formation, then to a

steady or unaltered condition of the ratio and finally to a reduction thereof.

A similar effect is produced by varying the quantity of coagulant incorporated into the latex. Thus, adding to  
70 the latex quantities of coagulant gradually increasing above the minimum quantity which is required to produce, as a result of the fermentation, a regularly  
75 cellulated mass, the value of the ratio referred to first increases and then rapidly decreases, while the coagulum becomes more and more hard, and the tendency of the serum to separate from the coagulum increasingly pronounced.  
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The precise quantities of fermentable substance and ferment in any given actual application of the invention, as also the most appropriate quantity of  
85 coagulating agent to be employed, will, in general, vary with the kind of rubber dispersion in hand, and with the water-content of the dispersion.

These quantities, however, can be  
90 readily determined by simple preliminary test.

The parent rubber dispersion may contain vulcanising and coagulating agents as already indicated, and in addition to  
95 these agents, if desired, fillers, dyestuffs, anti-oxidants or other addition substances common in the industry. It is to be appreciated, however, that care should be exercised to avoid the use of  
100 addition substances, notably certain accelerators, anti-oxidants and organic dyestuffs, the presence of which in the dispersion would tend to poison or weaken the action of the ferment.  
105

It is found that when sugars are used as the fermentable substance in conjunction with brewing ferments, the presence of sulphur for vulcanisation in the parent dispersion gives rise to the formation of  
110 hydrogen sulphide in the mass, this sulphide being evolved in addition to the carbon dioxide evolution from the fermentation. When a large quantity of sulphur is incorporated in the dispersion,  
115 for example, a quantity sufficient to result in the formation of ebonite, hydrogen sulphide is formed almost exclusively and only small quantities of carbon dioxide are evolved; and conversely, when only  
120 small quantities of sulphur are present, for example, such small quantities as are usually requisite to obtain soft rubber, the formation of hydrogen sulphide is correspondingly small and the evolution  
125 of carbon dioxide prevails, the amount of hydrogen sulphide formed being so small as to be readily capable of being bound, if necessary, by small quantities of zinc oxide suspended in the dispersion.  
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If the mix of parent rubber dispersion and fermentation substances contains only small quantities of added ingredients, for example, only vulcanising agents and zinc oxide, the bubble cells at the completion of fermentation may be of relatively large dimensions and the final elastic mass of cellular rubber may in consequence be incapable of quickly regaining its initial volume upon being compressed.

By incorporating a finely divided insoluble inert substance into the latex, however, for example, finely ground glass, pumice stone or siliceous material, the small particles of the incorporated substance function as centres or initiators of bubble formation and in this way, a vulcanised product may be produced which is highly resilient and constitutes an excellent sponge rubber, its cells being small and very regularly distributed.

It may further be remarked in this connection that the small and regularly distributed bubble cells which are produced in this manner readily intercommunicate with one another by rupture of their walls, after the step of vulcanising the coagulum, by heating the mould in which the fermentation has taken place.

In the contrary event, of additional finely divided solid matter, such as that referred to, being absent from the parent dispersion, the intercommunication of the bubble cells can be produced, either by immersing the fermented mass in boiling water for a sufficient time, vulcanising it, if necessary, at the same time, or by subjecting the coagulum to the action of a vacuum. The latter mode of operation may be carried out, either at room temperature, in which event subsequent heat treatment of the mass will be required to obtain a vulcanised product, or, alternatively, at an elevated temperature, the duration of the heat-treatment, in this case, being sufficient to effect, at the same time, dehydration and vulcanisation of the mass.

The quantity of bubble-promoting suspended solid matter in the dispersion may vary within fairly wide limits, for example, between 4 per cent. and 20 per cent. reckoned on the dry rubber content of the dispersion. In general, the higher the percentage of added solid matter employed, the more numerous and small will be the bubble cells in the finished product.

In the case of parent dispersions containing, for example, for the production of ebonite, relatively large quantities of sulphur, it may be unnecessary to incorporate additional finely divided solid matter in the dispersion for the promotion

of bubble formation, or at any rate such large quantities thereof as would otherwise be necessary, as in this case the evolution of gas occurs in the form of an exceedingly large number of small bubbles distributed throughout the mass of dispersion. This effect is probably due, either to the peculiar character of fermentation which occurs in the conditions contemplated, resulting, as stated, in the evolution of hydrogen sulphide in place of carbon dioxide, or to the presence in the dispersion of fine crystals of sulphur distributed through the mass and operating as initiating centres of bubble formation.

In this case also, after vulcanisation, the bubble cells are brought into intercommunication with one another upon application of heat or vacuum in the manner referred to above.

When the final products are of elastic rubber, such in general as those contemplated in the first of the following examples, a substantial decrease in volume of the bubble cells tends to occur during the drying of the coagulum, due to the contraction of the separating walls of the cells (which, as will be appreciated, are composed of more or less highly hydrated rubber) and in consequence, the resulting final products are more compact than the freshly formed coagulum and the cells may shrink in a somewhat irregular manner. We have found, however, that this effect may be avoided, if necessary, by preventing the outer surfaces of the mass of coagulum, as it is being dried and vulcanised, from contracting and thereby preventing general shrinkage of the cellular mass. By this means, the separating walls of the interior cells of the mass are compelled to dry without undergoing deformation or decrease in surface area and the initial open cellular structure of the wet coagulum is substantially preserved in the finished product.

One method of carrying this feature into effect consists in removing the fermented mass from the mould in which fermentation has taken place, preferably prior to the step of vulcanising the mass, and placing it into another mould, the walls of which are composed, like a cage, of metal network and have been previously coated with rubber solution or a like suitable adhesive. The cellular mass having been placed within this second mould, is then heated to vulcanise the component rubber. After this step, which can be carried out by placing the mould or cage into a closed container and immersing the whole into boiling water, the mould is immersed for a few hours

in cold water in order to cleanse the rubber within it, after which, still in position within the network cage, the cellular mass is dried, either in a vacuum or in a heated oven. Finally, the dried product is removed from the network mould and constitutes the finished product of the process.

As to the temperature to obtain in the fermentation step of the process, the most appropriate range of temperatures for most combinations of fermentable substances and ferment is from 25° to 36° C. When operating at 30°—31° C. with a dispersion containing the usual rubber mix ingredients and a small quantity of sulphur, for example, 2 to 7 per cent. reckoned on the dry rubber content of the mix, a maximum increase of superficial volume of the dispersion is reached in 6 or 7 hours the final volume then being about 4—5 times the initial volume of the parent mix. In the case of a mix containing a relatively high proportion of sulphur, for example, a proportion sufficient for the production of ebonite, the time required to attain maximum volume increase is considerably longer than in the former case, for example, twice as long, and the ultimate superficial volume reached somewhat less, for instance, only about 3—5 times the initial volume of the dispersion.

Generally speaking, as already stated, it is advisable, if not essential, substantially to free the rubber dispersion of ammonia before adding the fermentation materials, and it is probably equally important to ensure that decomposition of the proteins in the latex has not already begun when these materials are added.

According to a further feature of the invention, moreover, the actual degree of volume increase (or sponginess) in the cellulation of the dispersion may be controlled and predetermined by selecting a mould of an internal volume corresponding to the desired final volume of the coagulum and having in it, for example, at the top, an exit for the air displaced by the swelling of the mass, or for the escape of excess gas from the fermentation, and introducing into this mould for coagulation and fermentation therein just that quantity of parent dispersion which upon completion of fermentation will occupy the whole of the interior of the mould.

The invention will now be illustrated by way of guidance in the following Examples.

#### EXAMPLE I.

A parent rubber dispersion was prepared as follows :—

To 100 grams of latex, concentrated to 50 per cent. dry rubber content and freed from ammonia, there were added :

10 c.c. of a 50 per cent. solution of sugar having admixed with it 2 grams of yeast.

1.5 grams of crystallised magnesium sulphate and 1.5 grams of ammonium sulphate dissolved in 10 c.c. of water.

15 c.c. of a 5 per cent. aqueous solution of glue containing suspended in it 1 gram of sulphur, 0.5 grams of zinc dimethyldithiocarbamate, 0.2 grams of zinc oxide and 2 grams of very finely ground pumice stone.

This dispersion was left to ferment in a suitable mould for about 6 hours at about 30° C. The fermented mass was then removed from the mould and enclosed in another mould or cage having metallic mesh walls which had been previously coated with rubber solution. The second mould was placed in a closed container and the whole submerged into boiling water where it was left for about one-and-a-half hours for vulcanisation. During this step, the exterior surfaces of the mass remained steadily adhered to the network walls of the mould. The cage was then removed from the closed container and submerged for some hours in cold water, whereupon the mass was dried in a heated oven and the resulting final mass of sponge rubber was separated from the cage.

#### EXAMPLE II.

A parent dispersion for the production of sponge ebonite was prepared as follows :—

To 100 grams of latex of 50 per cent. dry rubber content previously freed from ammonia, there were added :

15 c.c. of a 50 per cent. solution of sugar containing admixed with it 1 gram of yeast.

4 grams of crystallized magnesium sulphate and 4 grams of ammonium sulphate dissolved in 35 c.c. of water.

20 c.c. of a 5 per cent. aqueous solution of glue containing suspended in it 17 grams of sulphur.

This dispersion was left to ferment in a suitable mould for about 6 hours at about 30° C. The mould containing the fermented mass was then heated in an autoclave for about 8 hours at a pressure of about 3 atmospheres (for example 143° C.) to effect vulcanisation of the mass. The final product was sponge ebonite having a very regular cellular structure.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we



claim is :—

1. A process for the manufacture of cellular rubber or ebonite or articles composed thereof, from aqueous rubber dispersions, characterised by gasifying the dispersion during coagulation thereof, with or without continuing the gasification after coagulation by effecting fermentation of material in the mass with evolution of gas therein.

2. A process as claimed in claim 1, comprising intimately admixing with a dispersion of rubber, for example, rubber latex, a solution of a fermentable substance and a solution or suspension of a ferment or its active principles, the fermentable substance and ferment being of a character such that gas is evolved by the fermentation which is insoluble or only slightly soluble in the dispersion.

3. A process as claimed in claim 1 or claim 2, comprising the additional step of heat-treating the cellular coagulum to rupture the walls of the cells thereof and thereby render them intercommunicating with one another.

4. A process for the manufacture of vulcanised cellular rubber or ebonite as claimed in any of the preceding claims, comprising the step of heat-treating the cellular coagulum to effect vulcanisation thereof.

5. A process for the manufacture of vulcanised cellular rubber or ebonite as claimed in claim 1 or claim 2, wherein the cellular coagulum is heat-treated to vulcanise it and at the same time rupture the walls of its cells.

6. A process as claimed in claim 4 or claim 5, wherein the parent rubber dispersion from which the coagulum is produced has vulcanising agents incorporated in it.

7. A process as claimed in any of the preceding claims, wherein the fermentable substance is glucose, cane sugar, beet sugar, molasses and the ferment is a saccharomyce of yeast or its enzymes.

8. A process as claimed in any of the preceding claims, wherein a coagulant is added to the parent rubber dispersion.

9. A process as claimed in claim 8, wherein the parent rubber dispersion consists of rubber latex depauperated of ammonia and there is added to said dispersion a coagulant for rubber latex in quantity less than that requisite to produce immediate coagulation of the dispersion and such that the coagulum which forms during fermentation of the fermentable material within the mass will first be substantially homogeneous and compact and then upon continued fermentation will swell due to further evolution of gas without the mass.

10. A process as claimed in claim 8 or claim 9, wherein the coagulant employed is magnesium sulphate.

11. A process as claimed in claim 10, wherein in order to prevent the immediate formation of precipitates within the dispersion produced by the action of the dissolved magnesium sulphate upon the albumens and other dissolved substances in the serum of the dispersion, an ammonium salt, for example, ammonium sulphate, is introduced into the dispersion, for example, is dissolved in the solution of magnesium sulphate.

12. A process for the manufacture of vulcanised cellular rubber or ebonite as claimed in any of the preceding claims, wherein for the purpose described a finely divided insoluble inert substance is incorporated into the latex, for example, finely ground glass, pumice stone or siliceous material.

13. A process as claimed in any of the preceding claims, wherein for the purpose described the outer surface of the mass of coagulum, as it is being dried and vulcanised, is prevented from contracting and thereby producing a general shrinkage of the mass.

14. A process as claimed in claim 13, wherein the prevention of contraction of the outer surface of the mass of coagulum is effected by removing the fermented mass from the mould in which fermentation has taken place, preferably prior to the step of vulcanising the mass, placing it into another mould, the walls of which are composed of metal network or the like previously coated with rubber solution or a like suitable adhesive for the coagulum, heat-vulcanising the mass in this mould, for example, by immersing it in boiling water, preferably immersing the vulcanised product still in position within the network mould in cold water to cleanse it and, finally, drying the cleansed cellular mass, still in position within the said mould, either in vacuo or by application of heat in the air.

15. A process as claimed in any of the preceding claims 1—8, wherein the parent dispersion employed is ammonia preserved rubber latex substantially depauperised of its ammonia content.

16. A process as claimed in any of the preceding claims, wherein the fermentation of the mass is effected in a mould having an internal volume corresponding to the desired final volume of the coagulum and provided, for example, at the top with an exit for the air which is displaced by the swelling of the mass or for the escape of excess gas evolved during the fermentation, and the quantity of parent dispersion which is introduced

into the mould is just that quantity which, upon completion of fermentation, will occupy the whole of the interior of the mould, the actual degree of volume increase (or sponginess) in the cellulation of the dispersion being thereby controlled and predetermined.

17. A process for the manufacture of cellular rubber or ebonite substantially as hereinbefore described in one or other of the specific examples given of the invention.

18. A process for the manufacture of

cellular rubber or ebonite substantially as hereinbefore described.

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19. Cellular rubber or ebonite when produced by a process as claimed in any of the preceding claims.

20. Articles, for example, moulded articles, composed of cellular rubber or ebonite as claimed in claim 19.

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